The Decompositions of *N*-(Substituted benzalamino)phthalimide Radical Cations Embody Ion-Neutral Complexes and Stevenson's Rule

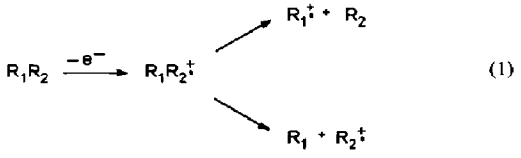
Cliffton B. Jacoby* and Michael L. Gross
Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska, Lincoln, Nebraska, USA

Robert L. Zey
Central Missouri State University, Department of Chemistry, Warrensburg, Missouri, USA

A previously unreported series of *N*-(substituted benzalamino)phthalimides was investigated by using the combined techniques of high resolution electron ionization mass spectrometry, metastable decomposition, and collisional activation mass spectrometry. The predominate fragmentation pathway is a McLafferty-type rearrangement. There also occurs, to a lesser extent, a transfer of hydrogen that originates from a substituent remote from the phthalimide moiety and terminates on the phthalimide. The process is interpreted as proceeding via an ion-neutral complex. The effects of substituents on both of the aforementioned fragmentation pathways provide a striking example that gives quantitative evidence for Stevenson's rule. The substituent effects are responsible for a trend in ion abundance that shows a sharp reversal at approximately the ionization energy of the iminium isomer of the phthalimide molecular ion. *(J Am Soc Mass Spectrom 1994, 5, 837–844)*

Ion decompositions in the gas phase can be described and predicted by using a number of arguments common to solution-phase chemistry. An early application of solution-chemistry principles to gas-phase ion chemistry was by McLafferty [1–3], who showed that the extent of fragmentation of a series of substituted benzoyl compounds correlates with the Hammett equation. Although such correlations are surprising because gas-phase ions that decompose at low pressure are not characterized by a temperature, they do indicate that principles that govern thermal processes also apply qualitatively to nonthermal processes.

The effect of substituents on the mass spectral behavior of an ion can be understood in another way as is illustrated in eq 1:



(1)

The relative abundance of ions R_1^+ and R_2^+ are determined by the ionization energies (IE) of the neutral molecules; usually the charged species whose neutral component has the lower IE predominates. This consideration, first recognized by Stevenson [4] in his work on a series of branched alkanes, is widely held and referred to as *Stevenson's rule*. Because the difference in ionization energies equals exactly the differences in the heats of formation of the two possible ion-neutral pairs, the rule is often recast today to state that the ion-neutral pair with the lower combined heats of formation will be preferentially formed. As one examines a series of compounds that differ only in substituents, one finds that ionization energy trends underlie substituent effects.

The relationship of ion abundances and ionization energies was probed for a variety of substituted aldehydes, ketones, alkanoic acids, methyl alkanoates, and amides by Meyerson and McCollum [5]. In their work, the energy dependence of the abundance of olefinic fragment ions formed by the McLafferty rearrangement was used to estimate the ionization energies of enolic fragment ions.

Ionization energies of substituted aromatics correlate with Hammett substitute (σ^+) values, and these correlations were established for a number of compounds such as benzyl derivatives [6], small substituted alkanes and cyclohexyl derivatives [7], mono-

Address reprint requests to Professor Michael L. Gross, Department of Chemistry, Washington University, One Brookings Drive, St. Louis, MO 63130.

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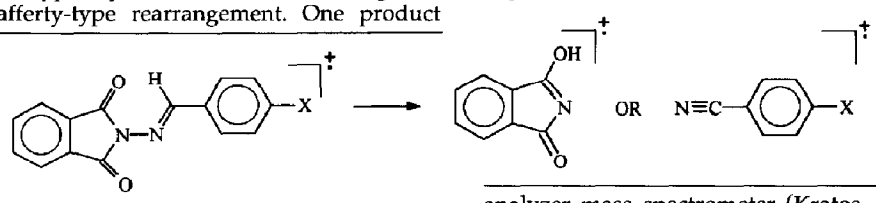
and disubstituted benzenes [8], diphenylethanes [9], phenols [10], and aldehydes [11]. Usually σ^+ constants give better correlations with ionization energies than do σ constants [12]. In contrast to the investigation of Meyerson and McCollum [5], all of these latter studies involved the formation of fragment ions through simple bond cleavage rather than by molecular rearrangement.

The focus of the work reported here is the mass spectra of a series of *N*-(4-substituted benzalamino) phthalimides. Typically, the molecular ions fragment via a McLafferty-type rearrangement. One product ion formed in this manner is likely to be the enol isomer of the phthalimide ion (see eq 2); the other may be a substituted benzonitrile radical cation. The electronic properties of a substituent X determines the relative abundances of these two product ions. The two products and particularly a third, protonated phthalimide, are formed via ion-neutral complexes. That Stevenson's rule and the concept of ion-neutral complexes are exemplified by the fragmentation chemistry of these phthalimides is the subject of this paper.



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Experimental

Materials

A series of *N*-(substituted benzalamino)phthalimides of the general structure shown in eq 2 were synthesized in the following manner. To 25 mL of absolute ethanol was added 6.00 mmol of *N*-aminophthalimide and 6.00 mmol of a 4-substituted benzaldehyde. The mixture was stirred and refluxed for approximately 5 h during which time a white solid separated. The mixture was filtered while hot to isolate the solid sample. This precipitate was recrystallized from ethanol or a mixture of ethanol and dimethylformamide. Sample purity was confirmed by the exhibition of sharply defined melting points. Structures were established by proton nuclear magnetic resonance. For this study, the substituents were H, CN, OH, F, Cl, Br, OCH_3, 2-CH_3, 3-CH_3, 4-CH_3, CH_2CH_3, $N(CH_3)_2$, $NHCOCH_3$, NO_2, COOH, $COOCH_3$, $COOCH_2CH_3$, OCH_2CH_3, and $OCOCH_3$.

To aid in the investigation of fragmentation pathways, two compounds with deuterated substituents, namely, —OD and —COOD, were also synthesized by repeated refluxing and recrystallization of the parent compounds from methyl alcohol-*d*. Complete exchange was never achieved; at best, 50% was obtained. Because the compounds were studied by tandem mass spectrometry, complete exchange was unnecessary.

Mass Spectrometry

Mass assignments and molecular formulae were confirmed by the high resolution electron ionization (EI) mass spectra obtained on a Kratos MS-50 double-analyzer mass spectrometer (Kratos Analytical, Ramsey, NJ) tuned to achieve a resolution of 10,000 (10% valley) and operating at 8-kV acceleration potential and 70-eV ionization energy.

All metastable ion decomposition spectra were obtained on a prototypal VG ZAB-T four-sector tandem mass spectrometer (VG Analytical Ltd., Manchester, UK) [13]. Parent ions were produced in an EI source with a filament current of 100 μA at 70 eV, and focused by the first-stage mass spectrometer (MS1) at a mass resolving power of approximately 1500 (10% valley) into the third field-free region of the instrument. Metastable product ions emerging from the interface region of MS1 and MS2 were focused at a resolving power of approximately 1000 [full width at half height (FWHH)]. MS2 was scanned over a mass range of m/z 400–30 in 20–30 s. Typically 10 scans were averaged together.

Collisional activation dissociation (CAD) spectra were obtained at mass resolving powers and instrument parameters as described above. Collisional activation was accomplished via the introduction of helium into the collision cell in the third field-free region between MS1 and MS2 at pressures sufficient to attenuate the parent ion beam by 50%.

The ionization energy of phthalimide was obtained on the Kratos MS-50 double focusing mass spectrometer equipped with an EI source containing a low-electron-volt filament and trap and tuned to a mass resolution of about 3000 (10% valley). To avoid auxiliary (Penning) ionization produced by electrons from the region around the filament trap, held at −35 V, and re-accelerated back into the source chamber, the ion repeller was adjusted to a sufficient negative potential to reduce the background to baseline when the ionizing potential was set below the onset of ion signals. The ionization energy of phthalimide was determined

relative to standards (toluene, benzene, and ethylene) with well-documented EI ionization energies (8.81, 9.25, and 10.5 eV, respectively) by using the semilogarithmic plot method [14].

Kinetic-energy-release spectra were measured on a Kratos MS-50 triple analyzer equipped with an EI source. This instrument was described previously [15]. Briefly, the molecular ion was selected and focused at a resolving power of approximately 1000 with MS1. Kinetic-energy-release spectra were recorded by scanning the second electrostatic analyzer in the mass-analyzed ion-kinetic-energy spectroscopy mode. The energy release values were measured at FWHH after correcting for the energy spread of the molecular ion beam.

Results and Discussion

The metastable ion spectrum of *N*-(benzalamino) phthalimide ion (Structure **1** in Scheme I) shows that the radical cation principally decomposes to give two fragment ions (see Figure 1). The molecular ion **1**, where X = H (*m/z* 250) undergoes McLafferty rearrangement to produce either an isomer of the phthalimide ion (Structure **2**, *m/z* 147) or the substituted benzonitrile radical cation (Structure **3**, *m/z* 103 for X = H), is shown in Scheme I.

Structures of Product Ions

Two possible isomers exist for the structure of the phthalimide ion, *m/z* 147, produced via the McLafferty rearrangement. Scheme I shows the hydrogen being transferred to the oxygen of the carbonyl group (iminium isomer, ion **2**); however, it is possible that the hydrogen is transferred to the imide nitrogen to form the phthalimide structure.

Unlike the CAD spectra of many keto–enol-type pairs, that of the radical cation produced via the McLafferty rearrangement in Scheme I differs significantly from the CAD spectrum of the radical cation of the phthalimide, produced via EI of authentic material

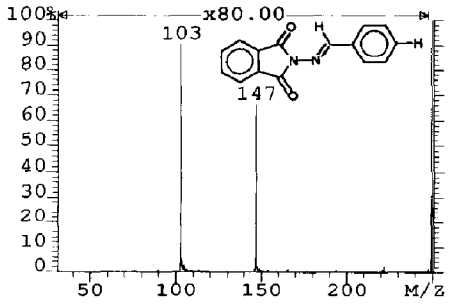
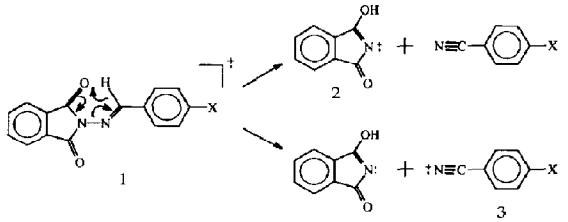


Figure 1. Metastable ion decomposition spectrum of *N*-(benzalamino)phthalimide.



Scheme I.

(see Figure 2a and b, respectively). The iminium isomer undergoes a facile loss of the hydroxy radical to produce the *m/z* 130 ion, which is likely to be the 2-cyanobenzoyl cation. This fragmentation is not detectable for the phthalimide ion owing to the necessity of 1,3-hydrogen transfer prior to expulsion of the hydroxy radical. Two other fragmentations of the iminium ion are also highly characteristic. The ion at *m/z* 105 can be formed by the expulsion of an NCO radical, a fragmentation pathway not seen for the phthalimide structure. The presence of the OH bond also allows for the loss of HCO_2, which gives the cation at *m/z* 102. The formation of this ion also may be explained by the concurrent loss of CO and the hydroxy radical, processes that are not likely to occur for the phthalimide structure.

Both the iminium isomer and phthalimide radical cations show the formation of the C_7H_4O ion at *m/z* 104, which is formed by loss of neutral HNCO. Possible skeletal rearrangements to facilitate these neutral and radical losses were suggested by Bentley and Johnstone [16, 17] and by Anderson et al. [18].

To prove that the substituted benzonitrile (3) is the structure of the other ionic product, CAD mass spectra were again used. The CAD spectra of the product radical cations were compared to those of commercially available benzonitriles that contain the substituents X = F, CH_3, OCH_3, CH_2CH_3, $N(CH_3)_2$, $NHCOCH_3$, and OCH_2CH_3. For this set of compounds, the spectra of 3 are nearly identical to those of authentic nitrile radical cations.

High Resolution EI Mass Spectra

The high resolution EI mass spectra of these *N*-(substituted benzalamino)phthalimide compounds confirm that the predominant fragmentation processes are those shown in Scheme I. As described above, the phthalimide radical cation typically undergoes further fragmentation to produce the ions at *m/z* 104 and 105 as well as the cyano-substituted benzoyl ion at *m/z* 130. In the cases where the benzonitrile radical cation is dominant, little subsequent fragmentation of this ion is seen. The fragments C_4H_2, C_5H_3, and C_6H_4 at *m/z* 50, 63, and 76, respectively, are produced as is expected for simple aromatic ions.

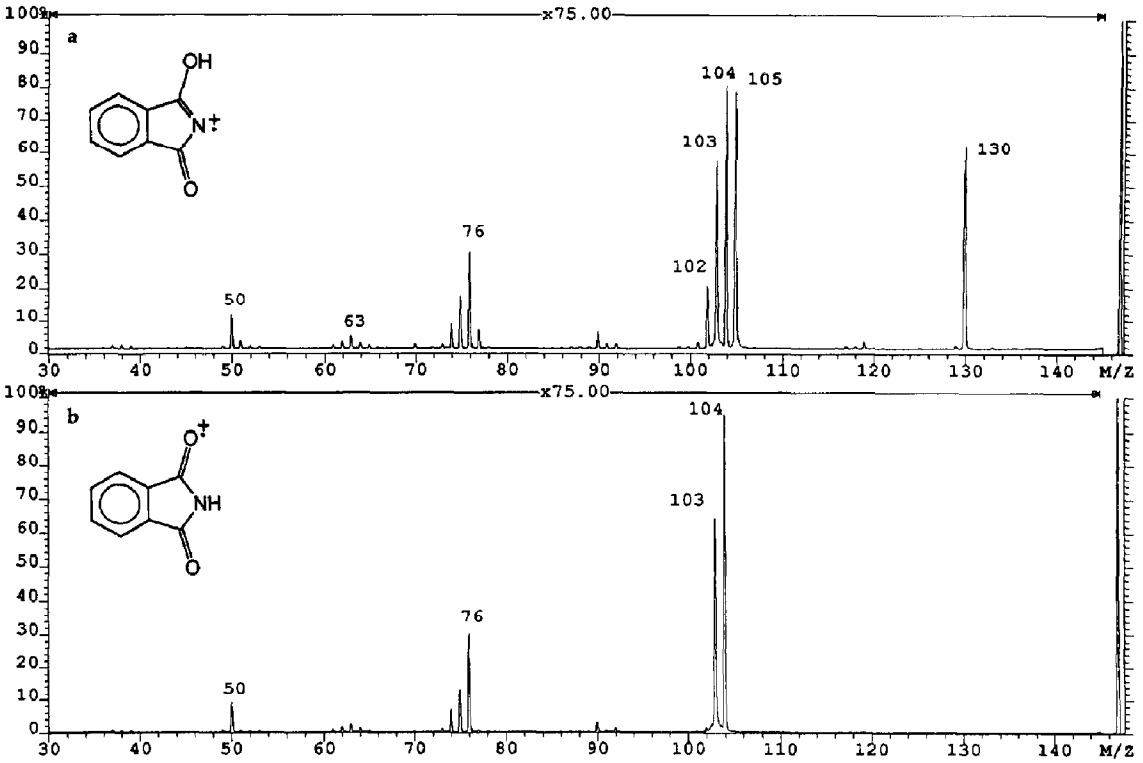


Figure 2. CAD spectra of the radical cations of (a) the iminium isomer of phthalimide and (b) phthalimide.

Substituent Effects

The mass spectra of the compounds investigated here can be grouped into two categories. The spectra of compounds that contain substituents with positive σ^+ values show that the most abundant fragment is the C_7H_5O ion of m/z 105, which we described earlier as coming from the loss of the NCO radical from the iminium radical cation. Those phthalimide compounds with substituents that have negative σ^+ values instead usually give the nitrile radical cations as the most abundant. This can be rationalized in terms of the low ionization energies of certain substituted benzonitriles and the lack of further fragmentation of the ionic forms of these species.

Although the nitrile radical cation is often formed most readily, a few exceptions occur. For the compound with X = 4-OH, the most abundant ion is the protonated phthalimide ion or (phthalimide + H)$^+$ at m/z 148. The rationale for this ion formation will be discussed later. The spectrum of the substituted phthalimide, where X = $NHCOCH_3$, shows a most abundant m/z 265 ion. The substituent group rearranges to expel ketene (CH_2CO), possibly via a four-membered transition structure, and gives the equivalent of *N*-(aminobenzalamino)phthalimide. The loss of CH_2CO is also seen for the compound where X = $-COCH_3$, as shown in eq 3, which results in a hydroxy-substituted material. Although the exact nature of fragment ions that arise from phenetole-type rearrangements is one of the classic problems in organic mass spectrometry [19–21], it is clear from the CAD spectra of the [M − CH_2CO] and the reference phenol radical cations that, at least in this case, the decomposing product ion possesses the phenol radical cation structure.

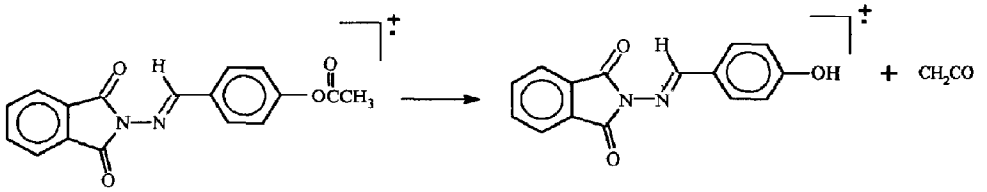


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Table 1. Ion abundances from high resolution electron ionization mass spectrometry[a]

X	σ^+	C_7H_4O	C_7H_5O	C_8H_4NO	$C_8H_5NO_2$	$C_8H_6NO_2$	XC_6H_4CN	Molecular ion
$N(CH_3)_2$	−1.7	10.2	3.0	3.2	2.4	N.D.	99.2	100.0
OH	−0.9	49.8	46.3	53.9	5.1	68.9	100.0	63.9
OCH_2CH_3	−0.8	40.1	27.1	13.2	3.8	4.0	100.0	93.6
OCH_3	−0.8	19.7	12.1	< 2	< 2	N.D.	100.0	20.6
$NHCOCH_3$	0.6	12.0	5.7	5.5	< 2	4.4	12.2	34.6
4-CH_3	−0.3	36.3	49.2	16.9	5.6	30.1	100.0	31.7
CH_2CH_3	−0.3	48.9	46.2	19.4	4.6	25.0	100.0	33.9
3-CH_3	−0.1	37.8	58.7	19.9	7.8	58.7	100.0	26.6
F	−0.1	54.5	100.0	6.0	23.3	< 2	54.8	16.3
2-CH_3	N/A	21.0	37.7	19.6	4.9	37.6	100.0	23.1
H	0.0	61.3	100.0	6.7	38.9	< 2	92.4	23.2
Cl	0.1	58.9	100.0	5.5	16.6	N.D.	58.8	16.6
Br	0.2	58.6	100.0	5.2	16.7	N.D.	35.7	4.8
$OCOCH_3$	0.2	31.1	29.8	32.3	5.5	N.D.	N.D.	12.9
COOH	0.4	56.0	100.0	14.8	78.7	28.2	78.7	11.7
$COOCH_2CH_3$	0.5	66.9	100.0	42.4	97.8	11.7	21.3	14.8
$COOCH_3$	0.5	58.0	100.0	55.8	39.6	< 2	49.4	15.0
CN	0.7	46.9	100.0	3.6	63.1	N.D.	5.7	10.2
NO_2	0.8	50.6	100.0	5.0	85.5	< 2	N.D.	7.3

[a]All data are corrected for ^{13}C contribution of ions one mass unit less. N.D. indicates no data and N/A denotes unavailable data.

The EI mass spectra in this series of *N*-(substituted benzalamino)phthalimides depend on the various substituents. For example, the compound with the substituent X = $N(CH_3)_2$, which has the most negative $\sigma^+(-1.7)$ of the substituents studied here, gives the most abundant molecular ion. The radical cation of the substituted benzonitrile is also quite abundant, as expected. The relative abundances of the fragment ions for the substituted compounds investigated here are tabulated according to molecular formulae in Table 1. For the compound substituted with —COOH, the exact masses for the nitrile and enol isomer are identical; therefore, it is impossible to differentiate the two ions by mass measurements only.

Substituent Effects and Stevenson's Rule

The direct competition between the formation of the phthalimide iminium isomer **2** and that of the substituted benzonitrile ion **3** in the McLafferty rearrangement (Scheme I) is a quantitative illustration of Stevenson's rule. The fragment whose neutral has the lower ionization energy always retains the positive charge. If the ionization energies are comparable, both products are seen, as in the metastable ion spectrum of the unsubstituted parent compound (see Figure 1).

Literature values for the ionization energy of benzonitrile range from 9.62 eV, determined by photoelectron spectroscopy (PES) [22, 23], to 10.02 eV, determined by EI. It is generally accepted that ionization energies from EI methods are higher than those determined by PES [24–27]. On the basis of the similar abundances of the fragment ions, the ionization energy of the neutral enol isomer of phthalimide should be in the range of 9.6–10.0 eV. This range of energies can be made smaller by studying a series of substituted compounds in which the ionization energy of the neutral form of the benzonitrile is altered via the use of substituent effects.

For various 4-substituted *N*-(benzalamino) phthalimides, the relative abundances of the substituted benzonitrile and the phthalimide isomer ions clearly depend on the substituent X and its electrical properties, for which the substituent constant σ^+ is a measure. Substituents with electron-donating properties (negative σ^+) lower the ionization energy, whereas electron-withdrawing groups raise it. The σ^+ values correlate roughly with the lowest reported ionization energies of para-substituted benzonitriles (correlation coefficient of 0.836; see Figure 3) [22, 23]. For

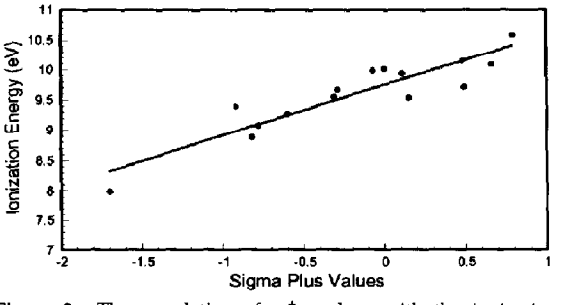


Figure 3. The correlation of σ^+ values with the ionization energies of para-substituted benzonitriles obtained from literature or from MNDO calculations.

the substituents $NHCOCH_3$ and CH_2CH_3, the values were calculated via MNDO and AM1. The validity of this approach was tested by computing the IE for all the substituted compounds and comparing, for the eleven compounds with known IE values, the experimental and theoretical values. Correlation coefficients of 0.965 and 0.966 were obtained for the modified neglect of differential overlap and AM1 results, respectively. The correlation of IE and σ^+ is surprisingly good given that the ionization energies were obtained by a variety of methods in different studies. It is also important to note here that the σ^+ value for the hydroxy group (—OH) in the para position is uncertain and may be closer to a value of -0.4 than to the accepted value of -0.92 [28, 29]. To our knowledge, this discrepancy has not been resolved.

Nevertheless, the correlation of σ^+ values and ionization energies of para-substituted benzonitriles offers an explanation for the relative abundances of ions **2** and **3** as the substituent is varied. For example, a strong electron-donating group such as 4-OCH_3 ($\sigma^+ = -0.78$) lowers the ionization energy of substituted benzonitrile so that, in accord with Stevenson's rule, ion **3** (4-methoxybenzonitrile, m/z 133) dominates the spectrum, as is seen in Figure 4a. In contrast, an electron-withdrawing group, such as 4-CN ($\sigma^+ = 0.66$) causes the spectrum to be dominated by the phthalimide isomer ion **2** (m/z 147), as is seen in Figure 4b.

Plotting the ionization energies of the neutral para-substituted benzonitriles versus the abundances of ion **3** relative to the sum of the abundances of ions **2** and **3** yields a well-defined sigmoidal curve (see Figure 5). From the sharp break of the titration-like curve in Figure 5, one notes the high sensitivity of the data to Stevenson's rule. Furthermore, the break in the curve should occur at the ionization energy of the enol isomer of the phthalimide ion; on that basis, the IE must be approximately 10.0 eV.

This type of sensitivity was also noted by Harrison et al. [30] for a system of substituted alkanes in which a change in ionization energy of 0.3 eV resulted in a complete change in appearance of the mass spectra.

Although there is, to our knowledge, no literature value for the ionization energy of the iminium isomer of phthalimide, the ionization energy of the phthalimide molecule previously had been determined by photoelectron spectroscopy to be 9.90 and 9.78 eV [31, 32]. We also measured the ionization energy of phthalimide via a modified semilogarithmic EI method whereby a low energy filament and trap were used (see Experimental). We obtained a value of 10.0 eV. Although these measurements pertain to the keto isomers, one expects the enol isomer (iminium ion) to have a similar IE. Thus, the measurement of 10.0 eV is consistent with the location of the break in the curve seen in Figure 5.

Ion Formation via an Ion-Neutral Complex

For compounds with substituents that have weakly acidic hydrogens (e.g., OH, 3-CH_3, 2-CH_3, 4-CH_3, COOH, and CH_2CH_3), an ion of m/z 148 with an exact mass in accord with the elemental formula $C_8H_6NO_2$ (within 5 ppm) was formed. This fragment is seen in the EI, CAD, and metastable ion spectra. Its presence in the metastable ion spectra indicates it is formed by a low energy process. The CAD spectrum of this ion and that of the $[M + H]^+$ of authentic phthalimide are nearly identical (for a discussion of the fragmentation of protonated phthalimide, see refs 16–18), which confirms that the C_8H_6NO fragment is

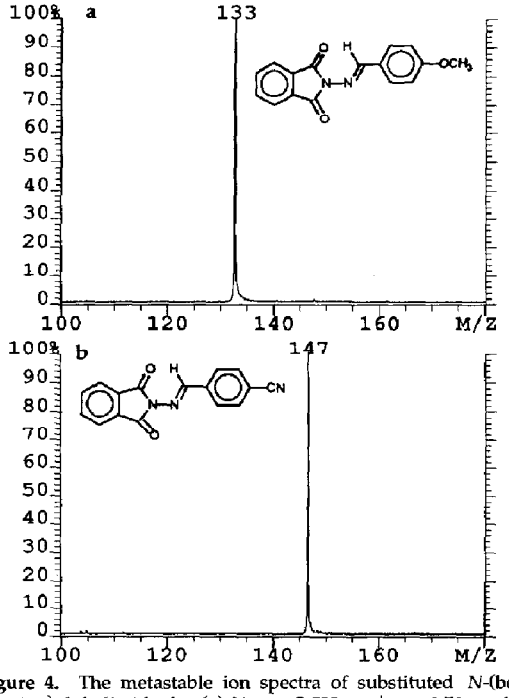


Figure 4. The metastable ion spectra of substituted *N*-(benzalamino)phthalimide for (a) X = $-OCH_3$, $\sigma^+ = -0.78$, and (b) X = $-CN$, $\sigma^+ = 0.66$.

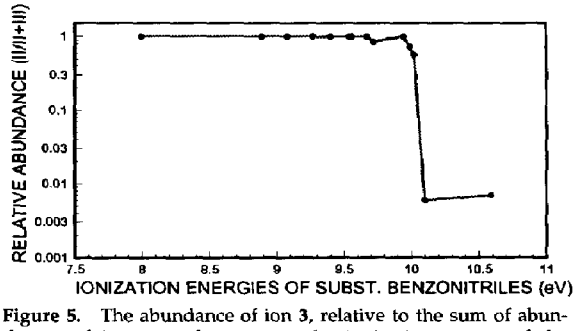
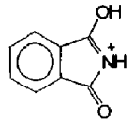


Figure 5. The abundance of ion **3**, relative to the sum of abundances of ions **2** and **3**, versus the ionization energy of the parasubstituted benzonitriles.

the protonated phthalimide (see Structure 4).



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Deuterium labeling studies with the OD and COOD substituents show that the hydrogen bound to the nitrogen of the imide group comes almost entirely from those substituents. The structure of the parent *N*-(benzalamino)phthalimide precludes the molecule folding back on itself to give H transfer. Rearrangement via an intermediate ion-neutral complex is the likely source of the $C_8H_6NO^+$ product.

Pioneering work in ion-neutral complexes has been done by Morton [33], who offered the following definition: "An ion-neutral complex is a non-covalently bonded aggregate of an ion with one or more neutral molecules in which at least one of the partners rotates freely in all directions." It is generally agreed that this complex is held together by the electrostatic attraction between the ion and the neutral molecule. The first proposal for the intervention of an ion-neutral complex in the dissociation of a molecular ion may be that of Rylander and Meyerson [34] in their work on the dissociation of alkyl benzenes. The subject of ion-neutral complexes was covered recently in a number of excellent reviews [35–39].

Many authors have proposed ion-neutral complexes to explain unusual hydrogen transfer and skeletal rearrangements [40–43]. Small complexes have been shown to be stable via ab initio calculations [44–46]. Convincing examples of ion-neutral complex formation in large systems were presented by Longevialle and Botter [47–49] in their work on difunctional steroids. They proposed that hydrogen transfers will be prevented if the initial fragments separate too rapidly, before the partners are capable of rotating into a proper orientation. Longevialle and Botter [47, 48] also suggested that, with increasing number of degrees of freedom, the average energy in the reaction coordinate will decrease and, in turn, increase the importance of complex formation.

Simple bond cleavage of an ion-neutral complex generally occurs with very small reverse activation energies and correspondingly small kinetic energy releases (below 10 meV). The kinetic energy releases in the formation of the protonated molecular ion of phthalimide of *m/z* 148 from the fragmentation of 4-methoxy, 4-methyl, and 2-methyl substituted phthalimides are 44, 38, and 38 meV, respectively. The alternative fragmentation of the 4-methyl-substituted compound to form the benzonitrile radical cation occurs with a kinetic energy release of 38 meV, and the formation of the iminium isomer of phthalimide in the decomposition of the 4-cyano compound takes place with a release of 31 meV. All these values are consistent with rate-determining steps in which a single bond is cleaved. They are also consistent with, but do not prove, intermediacy of a loosely bound complex.

The proposed mechanism that involves an ion-neutral complex (Scheme II) shows that as the first hydrogen is transferred and the nitrogen–nitrogen bond is broken, the benzonitrile radical cation fragment begins to separate, which allows it to rotate. For benzonitrile fragments that contain a substituent with an acidic proton, that proton is transferred, resulting in the formation of the protonated phthalimide and the neutral benzonitrile radical, which then separate with little kinetic energy release. When no acidic hydrogen is present, the complex simply separates into two fragments, and the charge is partitioned in accord with Stevenson's rule.

It is surprising, at least at first thought, that the abundances of the protonated phthalimide ($C_8H_6NO_2^+$) are comparable for the compounds with X = OH and CH_3 and significantly greater than for X = COOH. At issue here is the acidity of the substituted benzonitrile radical cation, not that of the neutral benzonitrile. For example, the calculated acidities of the phenol and toluene radical cations, which are taken as models for the corresponding *p*-methyl and *p*-hydroxybenzonitriles, are similar: 203 and 199 kcal/mol, respectively (see eqs 4 and 5):

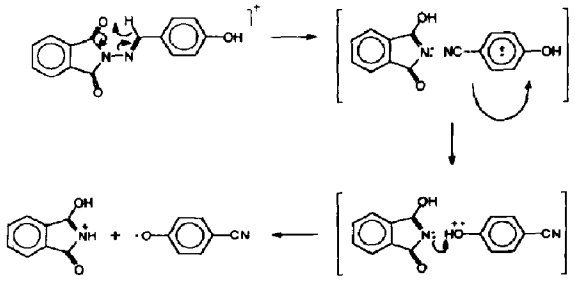
$$C_7H_8^+ \longrightarrow C_7H_7^\cdot + H^+ \qquad (4)$$

$$\text{and} \quad C_6H_5OH^+ \longrightarrow C_6H_5O^\cdot + H^+ \qquad (5)$$

In the ion-neutral complex that contains the 4-cyanobenzoic acid, the charge is nearly exclusively located on the phthalimide. Thus, it is the phthalimide radical cation that abstracts H from neutral 4-cyanobenzoic acid rather than the 4-cyanobenzoic acid radical cation that donates a proton to neutral phthalimide.

Miscellaneous Ion Formation

Aside from the unimolecular fragmentation pathways shown in Schemes I and II, some of the compounds undergo other fragmentations when ionized. For com-



Scheme II.

pounds with F, Cl, and Br substituents, losses of HF, HCl, and the chlorine and bromine radicals occur, as expected for halogenated compounds. The carboxylic acid-containing molecule shows small losses of the hydroxy radical as well as *i*-cleavage to eliminate the carboxy radical. The compound that contains the ethyl ester substituent undergoes a loss of the ethoxy radical as expected in addition to the loss (~15%) of C_2H_4. In the case of the methyl ester, the molecular ion undergoes *i*-cleavage to eliminate the methoxy radical.

Summary

The decompositions of a series of substituted *N*-(benzalamino)phthalimides are illustrative of concepts in contemporary gas-phase ion chemistry. These compounds decompose via ion-neutral complexes, at least at low energy, to give either a substituted benzonitrile or the iminium isomer of the phthalimide radical cation. The partitioning of charge is entirely consistent with Stevenson's rule. The product iminium radical cation does not interconvert with the phthalimide radical cation, even under conditions of high internal energy. When possible, the ion-neutral complex also undergoes proton transfer to give a protonated phthalimide, a species that requires, as an explanation for its formation, the intermediacy of an ion-neutral complex.

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